Electron-Probe Microanalysis: Instrumental Calibration, Standards, Quantitative Analysis, and Problem Systems

Paul Carpenter
Earth and Planetary Sciences
1 Brookings Drive
Washington University
St Louis, MO 63130
paulc@levee.wustl.edu
The Big Picture for EPMA

- Instrumental issues for EPMA:
  - Column-spectrometer alignment
  - Detector linearity and stability (flow, sealed)
  - WDS deadtime calibration
  - Spectrometer resolution, reproducibility
  - New developments: SDD EDS mapping and quantitative analysis

- EPMA Standards:
  - Proper selection of standards (sample vs. standard)
  - Internal consistency of stds in your lab vs. international environment

- Problem Systems:
  - Peak overlaps, high-order WDS interferences
  - Analytical problems, high absorption correction
  - Correction algorithms and mass absorption coefficient data sets

- Solutions:
  - Interlaboratory collaboration, education
  - Multiple KV and multiple spectrometer analysis of core std set
  - Payoff – proof of internal std comps and empirical macs
Washington University, Saint Louis
Earth and Planetary Sciences JEOL JXA-8200
Calibration Issues for Electron-Probe Microanalysis

• Microprobe performance specifications are:
  Driven by capabilities and address problem solving for customers
  Capabilities are funded by purchases, user/vendor development
  Realistic specifications for WDS vs. EDS systems

• Instrument calibration during installation and testing
  Spectrometer alignment – to electron column and mutual agreement
  Detector linearity with count rate and deadtime issues
  Precision = reproducibility (mechanical, electronic)
  Accuracy = correct K-ratio measured

• Instrument calibration – short vs. long term
  Consistent performance with time
  Accuracy in international interlaboratory environment

• Geological EPMA
  CMAS silicate standards used for acceptance testing (CIT, WU)
Pulse-Height Analysis
Wavelength-dispersive spectrometer
WDS PHA Measurement

• Low energy pulses must be discriminated from baseline noise. Need proper setting of noise threshold, baseline, and window settings of WDS pulse height analyzer.
• The pulse processing circuitry of WDS does not need to deal with pulse shaping like that of EDS, and is inherently faster.
• Pulse energy shift with varying count rate results in instability. At high count rates pulses are poorly discriminated from baseline noise. Use similar count rates on standard and sample.
• Avoid tight PHA window, use integral mode unless a PHA interference is observed.
• The P-10 detector gas flow rate must be stable or else gas amplification factor varies, and so does count rate.
• Temperature variation will affect gas amplification factor as well as thermal expansion of analyzer crystal.
• Low energy peaks need to be integrated due to peak centroid and peak shape/area factors. Use area-peak factor or perform integration.
Detector bias scan using 3.9 volt baseline and 0.2 volt window on PHA. Intended to minimize energy gain shift of PHA.

MSFC Spec 1, P-10 flow counter, TAP, 64x gain, Si Kα on SiO₂ metal @ 10k cps.
Detector PHA Scan Si Kα

For Si Kα there is good separation between baseline and Si pulses. Nominal baseline is 0.5 V with 9.5 V window (integral mode) MSFC Spec 1, P-10 flow counter, TAP, 64x gain, Si Kα on SiO₂ @ 10k cps.
Calibration of PHA
Using Bias vs. ln(E) plots

- For JEOL microprobe want SCA pulse at 4 volts, Cameca at 2 volts
- Spectrometer at peak position
- Bias scan with 3.8v base, 0.2v window gives bias for 4 volt SCA
- Plot of bias vs ln of x-ray energy is linear
- Calibration performed for minimum element set which spans energy range of spectrometer for all analyzing crystals
- Detector should give same bias for Ti Kα on PET vs. LIF, others
- Calibration confirms systematic behavior of x-ray counter
- As P-10 tank empties and Ar/CH₄ changes, requires recalibration
- Use $y = mx + b$ fit to bias data to provide quick calibration
- Similar plot for escape peak as function of x-ray energy
PHA Bias Plot for LIF/PET Data
Si, Ti, Ni Bias data at 8, 16, 32, 64, and 128x Gain

WU 8200 Detector Bias Spectrometer 3
Settings for 4 Volt Pulse

\[ y = -87.037x + 1955.1 \]
\[ y = -94.949x + 1889 \]
\[ y = -98.905x + 1808 \]
\[ y = -108.8x + 1748.9 \]
Gain shift due to count rate, detector bias arbitrarily set to 1700 volts. Observed shift is ~ 0.008 volts per 1 K cps (1.95 volt shift over 245 K cps range). At ~125k cps baseline noise discrimination deteriorates. Older PCS electronics exhibit complete shift into baseline noise. MSFC Spec 1, P-10 flow counter, TAP, 32x gain, Si Kα on Si metal.
Light element / low energy x-rays are poorly resolved from baseline noise. Gain shifts with count rate – PHA peak shifts toward baseline with increasing count rate. Use integral mode unless PHA energy discrimination required – counts extend to upper limit of PHA scan.

MSFC Spec 1 with P-10 flow counter, LDE2, 128x gain, Ti Lα on Ti metal @ 20k cps.
Carbon $K\alpha$ PHA Scans Graphite, Fe3C

Scaled PHA scans demonstrate consistent PHA behavior. No baseline – noise is present.

Graphite 100 nA > 65 kcps
Graphite 25 nA ~ 23 kcps
Fe3C 100 nA ~ 2 kcps

Baseline 0.5V, 9.5V Window

Baseline, Volts

Relative Intensity
Deadtime Measurement on the
Wavelength-Dispersive Spectrometer
WDS Deadtime Issues in EPMA

• Deadtime – time interval during which counting electronics are unable to process subsequent incoming pulses
• Deadtime error is non-negligible, systematic, affects all measurements
• General problem:
  • Counting behavior of WDS systems is undocumented and poorly known
  • End-users make measurements with assumed WDS deadtime behavior
  • User knowledge of deadtime issues needs improvement
• Specific problem areas:
  No software to conveniently evaluate deadtime on turnkey systems
  No agreed method for setting bias, gain, and sca on systems
  SCA pulse shift behavior with count rate undocumented
  Deadtime dependence on X-ray energy undocumented and unknown
  Low vs. high count rate behavior and deadtimes inconsistent
Deadtime Behavior:
Extending vs. Nonextending

Nonextending: \[ N = N_m (1 - N \tau), \quad N_{\text{max}} = \frac{1}{\tau} \]

Extending: \[ N = N_m e^{-N_m \tau}, \quad N_{\text{max}} = \frac{1}{e\tau} \]
Deadtime Losses
Input – Output Curves for μsec Deadtime Constants
Percentage Deadtime Losses
Percent Level Corrections Apply to All Measurements

At 1 μsec, 1% correction at 10Kcps, 5% at 50Kcps
At 2 μsec, 2% correction at 10Kcps, 10% at 50Kcps

~1.25 μsec
Deadtime Relations
Calculation of Deadtime Constant

\[ N = \frac{N_m}{(1 - N_m \tau)} \]

- \( N \) = true count rate, \( N_m \) = measured count rate with
deadtime losses (\( N_m < N \)), and \( \tau \) is the deadtime constant,
which ranges from 1 to several \( \mu \)sec for WDS counting
systems. It is necessary to know \( N_m \) and \( N \) to calculate \( \tau \).
We assume the proportionality of \( N \) to the probe current \( i \)
is constant. This may not be true at low count rates.

\[ \frac{N_m}{i} = c(1 - N_m \tau) \]

- \( \frac{N_m}{i} \) = measured count rate in counts per second per nA,
and \( c \) is the constant \( N / i \)
Form: \( y = mx + b \)
(\( \frac{N_m}{i} \)) is \( y \), \( x \) is \( N_m \), \( y \)-intercept \( b \) is constant \( c \) (= \( N / i \)).

\[ \tau = \frac{[1 - (N_m/i)/c]}{N_m} \]

- Equivalent to \( \tau = (1 - y/b)/x \)
Measure x-ray intensity at increasing probe current
Use count rate \( N_m \) and \( N_m / i \) to evaluate the deadtime
constant \( \tau \) over a range of intensity values
Deadtime Evaluation Plot

\[ N_m \text{ vs. } N_m/i \text{ to determine LS Fit to } \tau \]

\[
N = \frac{N_m}{(1 - N_m \tau)}
\]

\[
\tau = \frac{[1 - (N_m/i)/c]}{N_m}
\]
Verification of Probe Current vs. Absorbed Current Linearity and/or Detection of Sample Charging

Identification of Sample Charging:
Ratio of Absorbed Current to Probe Current

- Conductive Si Wafer
- Conductive Si Wafer Run 2
- Charging Si Wafer
Deadtime Calculation from Excel Spreadsheet

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<tr>
<th>nA</th>
<th>Abs Cur</th>
<th>Abs/Prob</th>
<th>Time</th>
<th>Cps (x)</th>
<th>Cps/nA (y)</th>
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Regression Output:
- Mean deadtime: 0.86 0.84
- All Y intercept: 2309.01 Slope: -0.0020 Sigma: 0.02 0.01
- High CR Y intercept: 2304.04 Slope: -0.0019 Regression DT: 0.87 0.84

Excel Sheet: X is $N_m$ and Y is $N_m/i$. Deadtime evaluated from each intensity (DT) and from least squares fit to data (Fit) using Excel *linest* function. All data and high intensity only data are compared with average values (Mean deadtime) and standard deviation. Ratio of absorbed/probe current checks conductivity. If linear all data agree.
Deadtime Variation with Count Rate

Caltech 733 Spec 2 with P-10 flow counter
Deadtime at low count rates include dark current and are not representative of dynamic range of spectrometer
Deadtime Variation With Time and P-10 Gas Chemistry Comparison of Original and New Tracor PCS Electronics
Alignment and Quantitative Analysis:
Wavelength-Dispersive and Energy-Dispersive Spectrometers
Establishing Calibration of an Electron Microprobe

- Wavelength spectrometer aligned vertically (baseplate) to coincide with optical microscope focal point in z-space
- Diffracting crystal aligned to be on Roland circle
- All WDS should focus on same z-axis and coincident xy area ~ 50 um in diameter
- Characteristics of correct alignment
  - All WDS & EDS have identical X-ray takeoff angle
  - Maximum X-ray intensity at z focus position, but also require:
    - Measure identical k-ratio within counting statistics
- Simultaneous k-ratio measurement is ultimate test of alignment
- Initial CMAS standard set used on Caltech MAC and JEOL JXA-733
- Expanded CMASTF standard set used for Wash U JXA-8200
Electron Microprobe Column
Spectrometer Alignment: Baseplate and Crystal

**Baseplate**: Place Rowland circle at Z focus

**Crystal**: Align all crystals on Rowland circle

Spectrometer design keeps detector on RC

Note: Different K-ratio = misalignment

Multiple spectrometer comparison required to demonstrate all WDS and EDS are mutually aligned
CMASTF Silicate Standards
Geological materials are multicomponent

• End-member stoichiometric silicate and oxide mineral standards
• Primary standards:
  MgO, Al₂O₃, SiO₂, CaSiO₃ (CaO 48.27, SiO₂ 51.73), TiO₂, and Fe₂O₃
• Analyzed suite of stoichiometric standards, natural and synthetic materials:
  Second set of primary standards on different mounts
  Spinel MgAl₂O₄, Enstatite MgSiO₃, Forsterite Mg₂SiO₄
  Kyanite Al₂SiO₅
  Fayalite Fe₂SiO₄
• Well characterized natural mineral standards and glasses:
  Olivines (Mg,Fe)₂SiO₄
  Diopside CaMgSi₂O₆, Anorthite CaAl₂Si₂O₈, Sphene CaTiSiO₅
  Ilmenite FeTiO₃
  Synthetic glasses in CMAS and CMASF system:
  Weill CMAS glasses, NBS K411, K412
## CMASTF Standard Inventory: Natural & Synthetic Composition in Wt% Oxide

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<tr>
<th>Standard</th>
<th>MgO</th>
<th>Al2O3</th>
<th>SiO2</th>
<th>CaO</th>
<th>TiO2</th>
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UO EPMA Workshop 2008
Pouchou Experimental Binary K-ratio Data Set (n=756) 
Φ(ρz) Algorithm – No silicates or multi-element materials 

Average $K^{corr} / K^{exp} = 1.0079 +/- 0.0382 (1 \sigma)$
Ag Lα NIST SRM 481 AgAu Alloy ($\psi=40$)

$C$ vs. $C / K$ plot for Ag Lα data

$y = mx + b$

$\alpha$ factor is $b$ intercept

slope is $1 - \alpha$

$C / K$

$C$ Ag, weight fraction
Accuracy Study for EPMA
Comparison of Measured to Calculated K-ratio

\[ K_{\text{measured}} = \frac{(P - B)_{\text{sample}}}{(P - B)_{\text{standard}}} \]

\[ C = K \times ZAF \]

\[ K_{\text{calculated}} = \frac{C}{ZAF} \]

Evaluate: \( \frac{K_{\text{measured}}}{K_{\text{calculated}}} \)

- \( K_{\text{measured}} \) dependent on:
  - Accelerating Potential
  - Probe current
  - Detector (gas, sealed)
  - Pulse processing
  - PHA calibration
  - Deadtime
  - Spectrometer alignment
  - Sample homogeneity
  - P-B determination, stripping, counting statistics
  - Other sampling/drift factors

- \( K_{\text{calculated}} \) dependent on:
  - Correct composition of standard
  - Correction algorithms
  - Data sets, mass absorption coefficients
  - Other algorithmic factors
Historical CMAS Data
Caltech MAC Probe, Circa 1980’s

Shaw Data Set: Caltech MAC Probe (38.5 deg, 15 kV)
Armstrong $\phi(\rho z)$, FFAST macs
Caltech JEOL 733 1990’s
Spectrometer 1 TAP for Mg Al Si (Ca PET)

Shaw Data Set: Caltech Jeol 733 -- TAP1 MgAlSi PET3 Ca
Armstrong $\phi(\rho z)$, FFAST mags, 15 kV

Weight % Oxide

Measured Wt% / Accepted Wt%

- Mg
- Al
- Si
- Ca
Caltech JEOL 733 1990’s Spectrometer 2 TAP for Mg Al Si (Ca PET)

Shaw Data Set: Caltech Jeol 733 -- TAP2 MgAlSi PET5 Ca
Armstrong $\phi(\rho_z)$, FFAST macs, 15 kV
Caltech JEOL 733 1990’s
Spectrometer 4 TAP for Mg Al Si (Ca PET)

Shaw Data Set: Caltech Jeol 733 -- TAP4 MgAlSi PET5 Ca
Armstrong $\phi(\rho z)$, FFAST macs, 15 kV
Caltech JEOL 733 1990’s
Spectrometer 124 TAP for Mg Al Si (Ca PET)

Shaw Data Set: Caltech Jeol 733 -- TAP124 MgAlSi PET35 Ca
Armstrong $\phi(\rho z)$, FFAST macs, 15 kV

Measured Wt% / Accepted Wt%

Mg, Al, Si, Ca
Caltech JEOL 733 1990’s
Spectrometer 124 TAP for Mg Al Si (Ca PET)

Shaw Data Set: Caltech Jeol 733 -- TAP:1Mg 2Al 4Si
Armstrong φ(ρz), FFAST macs, 15 kV
# Intercomparison of Measured vs. Accepted Concentration for Standards on Microprobes

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<th>Instrument</th>
<th>$C_{\text{meas}}/C_{\text{calc}}$ Mg</th>
<th>$C_{\text{meas}}/C_{\text{calc}}$ Al</th>
<th>$C_{\text{meas}}/C_{\text{calc}}$ Si</th>
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<td>0.9984</td>
</tr>
<tr>
<td>Caltech 733 MgAl2Si4, 1sd</td>
<td>0.0077</td>
<td>0.0188</td>
<td>0.0061</td>
<td>0.0063</td>
</tr>
</tbody>
</table>
WU JXA-8200 CMASTF Data Set
All WDS Data Superimposed
WU JXA-8200 CMASTF Data Set
Spectrometer 1 PET and TAP

\[ \frac{K_{\text{meas}}}{K_{\text{calc}}} \]

Oxide Weight Percent

\[ 0 \quad 10 \quad 20 \quad 30 \quad 40 \quad 50 \quad 60 \quad 70 \quad 80 \quad 90 \quad 100 \]
WU JXA-8200 CMASTF Data Set
Spectrometer 2 TAP
WU JXA-8200 CMASTF Data Set
Spectrometer 3 PET and LIF

\[ \frac{K_{\text{meas}}}{K_{\text{calc}}} \]

Oxide Weight Percent

\[ 0 \quad 10 \quad 20 \quad 30 \quad 40 \quad 50 \quad 60 \quad 70 \quad 80 \quad 90 \quad 100 \]
WU JXA-8200 CMASTF Data Set
Spectrometer 4 PET and LIF

\[ \frac{K_{\text{meas}}}{K_{\text{calc}}} \]

Oxide Weight Percent
WU JXA-8200 CMASTF Data Set
Spectrometer 5 PETH and LIFH

oxide weight percent

K_{meas} / K_{calc}

Oxide Weight Percent
## Average $K_{meas} / K_{calc}$ for CMASTF Standards

Washington University JEOL 8200

<table>
<thead>
<tr>
<th>WDS</th>
<th>Spec 1</th>
<th>Spec 2</th>
<th>Spec 3</th>
<th>Spec 4</th>
<th>Spec 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg TAP</td>
<td>0.9997</td>
<td>0.9971</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al TAP</td>
<td>0.9950</td>
<td>0.9946</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si TAP</td>
<td>0.9981</td>
<td>0.9955</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si PET</td>
<td>0.9855</td>
<td></td>
<td>0.9865</td>
<td>0.9837</td>
<td>0.9880</td>
</tr>
<tr>
<td>Ca PET</td>
<td>1.0013</td>
<td></td>
<td>1.0064</td>
<td>1.0035</td>
<td>1.0101</td>
</tr>
<tr>
<td>Ca LIF</td>
<td></td>
<td></td>
<td>0.9908</td>
<td>0.9948</td>
<td>0.9989</td>
</tr>
<tr>
<td>Ti PET</td>
<td>1.0000</td>
<td></td>
<td>1.0059</td>
<td>1.0044</td>
<td>1.0115</td>
</tr>
<tr>
<td>Ti LIF</td>
<td></td>
<td></td>
<td>0.9919</td>
<td>0.9949</td>
<td>1.0084</td>
</tr>
<tr>
<td>Fe LIF</td>
<td></td>
<td></td>
<td>0.9962</td>
<td>1.0051</td>
<td>1.0131</td>
</tr>
</tbody>
</table>
### Accuracy, 1σ % Error in $K_{\text{meas}} / K_{\text{calc}}$ CMASTF Standards  Washington University JEOL 8200

<table>
<thead>
<tr>
<th>WDS</th>
<th>Spec 1</th>
<th>Spec 2</th>
<th>Spec 3</th>
<th>Spec 4</th>
<th>Spec 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg TAP</td>
<td>0.65</td>
<td>1.30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al TAP</td>
<td>1.06</td>
<td>1.22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si TAP</td>
<td>0.74</td>
<td>0.64</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si PET</td>
<td>0.71</td>
<td></td>
<td>0.71</td>
<td>0.75</td>
<td>0.70</td>
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<tr>
<td>Ca PET</td>
<td>0.79</td>
<td></td>
<td>0.73</td>
<td>0.70</td>
<td>0.74</td>
</tr>
<tr>
<td>Ca LIF</td>
<td></td>
<td></td>
<td>0.74</td>
<td>0.92</td>
<td>0.69</td>
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<tr>
<td>Ti PET</td>
<td>2.27</td>
<td></td>
<td>1.44</td>
<td>0.98</td>
<td>1.54</td>
</tr>
<tr>
<td>Ti LIF</td>
<td></td>
<td></td>
<td>0.61</td>
<td>1.15</td>
<td>1.14</td>
</tr>
<tr>
<td>Fe LIF</td>
<td></td>
<td></td>
<td>1.75</td>
<td>1.27</td>
<td>1.26</td>
</tr>
</tbody>
</table>
WU JXA-8200 CMASTF Data Set
All WDS Data Superimposed Expanded Scale

Oxide Weight Percent

K_{meas} / K_{calc}
Washington University
Earth and Planetary Sciences JEOL JXA-8200 SDD

JEOL e2v Silicon Drift Detector
130 eV resolution
3 time constants T3 T2 T1
Stage and beam mapping
Quantitative EDS analysis LLSQ
JEOL 8200 Stage Maps: Lunar Meteorite SAU169
WDS vs. SDD Mg @ 15KV, 120nA, 25ms dwell

Mg WDS 1061 max counts, Mg SDD 527 max counts
1024x1024 stage map, 8 hours
Lunar Meteorite SAU169
Stage map 1024x1024, 25 ms, 8 hr run

Backscattered electron vs. Fe SDD maps
Lunar Meteorite SAU169
Stage map 1024x1024, 25 ms, 8 hr run: Ca SDD
WU8200 JEOL SDD
$^{55}$Fe Source Mn Kα Resolution 130 eV

Washington University JEOL 8200
SDD Mn Spectra T3 15 KeV, 100 sec
$^{55}$Fe Source ~255 Cps 0.27% Deadtime

Counts per 100 sec

Energy, KeV

300nA T3
200nA T3
150nA T3
100nA T3
50nA T3
25nA T3
10nA T3
Mn 55Fe

140k cps
125k cps
110k cps
80K cps
50k cps
25k cps
10K cps
SDD Performance Data:
WU8200 SDD Mn Target, T1 15 KeV, 100 sec

Washington University JEOL 8200
SDD Mn Spectra T1 15 KeV, 100 sec

Counts per 100 sec

Energy, KeV

210k cps
150k cps
125k cps
80K cps
50k cps
25k cps
10K cps
SDD Performance Data:
WU8200 SDD Mn Target, T3 15 KeV, 100 sec

![Graph showing SDD Mn Spectra T3 15 KeV, 100 sec]

Counts per 100 sec:
- 300nA T3: 140k cps
- 200nA T3: 125k cps
- 150nA T3: 110k cps
- 100nA T3: 80K cps
- 50nA T3: 50k cps
- 25nA T3: 25k cps
- 10nA T3: 10K cps

Energy, KeV:
- 0
- 5
- 10
- 15
- 20

Washington University JEOL 8200
SDD Mn Spectra T3 15 KeV, 100 sec
WU8200 SDD Mn K Spectra
T3, 100 sec
WU8200 SDD Mn K Spectra
T1, 100 sec
WU8200 SDD Mn L Spectra
T3, 100 sec

Washington University JEOL 8200
SDD Mn Spectra T3 15 KeV, 100 sec

Normalized Intensity

Energy, KeV

Normalized Intensity

Energy, KeV

140k cps
125k cps
110k cps
80K cps
50k cps
25k cps
10K cps
WU8200 SDD Mn L Spectra
T1, 100 sec

Washington University JEOL 8200
SDD Mn Spectra T1 15 KeV, 100 sec

Normalized Intensity

0.00 0.25 0.50 0.75 1.00 1.25 1.50

Energy, KeV

0.0 0.2 0.4 0.6 0.8 1.0

210k cps
150k cps
125k cps
80K cps
50k cps
25k cps
10K cps
WU8200
Probe Current vs. Count Rate

![Graph showing the relationship between probe current and count rate for WU8200 JEOL SDD. The x-axis represents probe current in nA, and the y-axis represents counts per second full range. Three lines are plotted for T1 Cps, T2 Cps, and T3 Cps.]
Washington University JXA-8200 SDD
Deadtime vs. Count Rate

Counts per Second vs. Dead Time

- T1
- T2
- T3
WU8200 SDD
Count Rate vs. Resolution

Washington University JXA-8200 SDD
Mn Resolution vs. Cps @ T1 - T3
**WU8200 SDD**

**Count Rate vs. Resolution for C, Si, Mn, Ni**

**Washington University JXA-8200 JEOL SDD**

**Energy Resolution vs. Input Count Rate @ T3**

- **Ni:** \( y = 7 \times 10^{-5}x + 144.11 \)
- **Mn:** \( y = 7 \times 10^{-5}x + 129.75 \)
- **C:** \( y = -2 \times 10^{-6}x + 121.46 \)
- **Si:** \( y = 6 \times 10^{-5}x + 84.43 \)
Washington University JXA-8200 SDD
Corning 95IRV: K, Ti, Cr, Fe, Ce, Hf

Washington University JXA-8200 SDD
Corning 95-Series Trace Element Glasses @ 15 KeV, 50 nA

Energy, KeV

Counts

O, Mg, Al, Si

Ca

K, Ti, Ce, Cr, Fe, Hf
Washington University JXA-8200 SDD
Corning 95IRW: V, Mn, Co, Cu, Cs, Ba, La, Th

Washington University JXA-8200 SDD
Corning 95-Series Trace Element Glasses @ 15 KeV, 50 nA

Energy, KeV

Counts

0 1 2 3 4 5 6 7 8 9 10

1 1000000

100000

10000

1000

100

10

1

O, Mg, Al, Si

Ca

Th, Ba

V, Mn

La

Co

Cu
Washington University JEOL JXA-8200
SDD Quantitative Analysis Data

• SDD great for mapping, what about quantitative analysis?
• SDD EDS data acquired at 120s, 60s, and 3s acquisitions at T3
• Standards used: MgO, Al₂O₃, SiO₂, CaSiO₃ (CaO 48.27, SiO₂ 51.73), TiO₂, and Fe₂O₃
• Linear least-squares peak deconvolution (JEOL software)
• Extracted raw K-ratios processed using Armstrong $\Phi(\rho z)$ and FFAST macs for comparison with WDS data
CMASTF Standard Analyses
WU8200 SDD LLSQ 120 sec. Acquisition T3

Measured K Relative to Calculated K
WU8200 SDD 120 sec Acquisition

- Mg Km/Kc
- Al Km/Kc
- Si Km/Kc
- Ca Km/Kc
- Ti Km/Kc
- Fe Km/Kc

Weight Percent Oxide
CMASTF Standard Analyses
WU8200 SDD LLSQ 60 sec. Acquisition T3

Measured K Relative to Calculated K
WU8200 SDD 60 sec Acquisition

Weight Percent Oxide

Km / Kc

Mg Km/Kc
Al Km/Kc
Si Km/Kc
Ca Km/Kc
Ti Km/Kc
Fe Km/Kc
CMASTF Standard Analyses
WU8200 SDD LLSQ 3 sec. Acquisition T3

Measured K Relative to Calculated K
WU8200 SDD 3 sec Acquisition

Weight Percent Oxide

Mg Km/Kc
Al Km/Kc
Si Km/Kc
Ca Km/Kc
Ti Km/Kc
Fe Km/Kc
## Average Kmeas / Kcalc for CMASTF Standards
### WU8200 SDD Data @ 120, 60, 3 sec acquisition T3

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Ca</th>
<th>Ti</th>
<th>Fe</th>
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<tr>
<td><strong>120s Data</strong></td>
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<td></td>
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</tr>
<tr>
<td>Average</td>
<td>1.0122</td>
<td>1.0064</td>
<td>1.0017</td>
<td>0.9926</td>
<td>1.0021</td>
<td>1.0108</td>
</tr>
<tr>
<td>1 σ</td>
<td>0.0063</td>
<td>0.0122</td>
<td>0.0078</td>
<td>0.0066</td>
<td>0.0106</td>
<td>0.0140</td>
</tr>
<tr>
<td>Relative %</td>
<td>0.62</td>
<td>1.21</td>
<td>0.78</td>
<td>0.67</td>
<td>1.06</td>
<td>1.38</td>
</tr>
<tr>
<td><strong>60s Data</strong></td>
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</tr>
<tr>
<td>Average</td>
<td>1.0058</td>
<td>1.0022</td>
<td>0.9969</td>
<td>0.9895</td>
<td>0.9975</td>
<td>1.0083</td>
</tr>
<tr>
<td>1 σ</td>
<td>0.0118</td>
<td>0.0162</td>
<td>0.0069</td>
<td>0.0066</td>
<td>0.0150</td>
<td>0.0113</td>
</tr>
<tr>
<td>Relative %</td>
<td>1.17</td>
<td>1.61</td>
<td>0.69</td>
<td>0.67</td>
<td>1.51</td>
<td>1.12</td>
</tr>
<tr>
<td><strong>3s Data</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Average</td>
<td>1.0061</td>
<td>1.0135</td>
<td>1.0001</td>
<td>0.9933</td>
<td>0.9947</td>
<td>1.0123</td>
</tr>
<tr>
<td>1 σ</td>
<td>0.0162</td>
<td>0.0263</td>
<td>0.0104</td>
<td>0.0213</td>
<td>0.0118</td>
<td>0.0211</td>
</tr>
<tr>
<td>Relative %</td>
<td>1.61</td>
<td>2.59</td>
<td>1.04</td>
<td>2.14</td>
<td>1.19</td>
<td>2.09</td>
</tr>
</tbody>
</table>
EPMA Standards
Advances in EPMA:
Geological Materials -- Standards

• EPMA standards requirements: Homogeneous on micron scale, grain to grain, well characterized on both scales, and available in large enough quantity to be used by microanalysis communities.
• Most materials fail one or more of these requirements.
• Natural and synthetic minerals, oxides, and glasses.
  Minerals impose stoichiometry but may be inhomogeneous
  Glasses lack stoichiometric control but can be homogeneous
• Glasses: targeted compositions that can be made in bulk and utilized by the microanalysis community.
  (Corning 95-series trace element glasses)
• Internal consistency of EPMA standards used by the community is poorly known. Few comparison reports, generally anecdotal.
• Solution: calculate expected x-ray intensity for element of interest in suite of standards, compare measured intensities relative to end-member standard (oxide), i.e., \( k = \frac{ZAF}{C} \). This highlights errors in composition as well as systematic errors in algorithm.
Basalt Glass Indian Ocean USNM 113716: EPMA vs. Wet Chemistry Data

Of the 3-5 mounts of UNSM 113716, this is the first observation of mineral inclusions or crystallites in the glass. This is otherwise a homogeneous standard, consistent with EPMA of other glasses, but based on wet chemistry comparison. 

How representative is this of the wet chemical analysis?
Olivine Standards: Mg-rich (Mg,Fe)$_2$SiO$_4$

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Shankland forsterite Fo$_{100}$</td>
<td>Synthetic</td>
<td>Fe?</td>
</tr>
<tr>
<td>Boyd olivine Fo$_{93}$</td>
<td>Natural</td>
<td>Mn, Co, Ni, Zn?</td>
</tr>
<tr>
<td>LLNL “Fo85” (Fo$_{93}$)</td>
<td>Synthetic</td>
<td>&lt;none&gt;</td>
</tr>
<tr>
<td>San Carlos olivine Fo$_{90}$</td>
<td>Natural</td>
<td>Na?, Mg, Al, Ca, Ti?, Cr, Mn, Co, Ni</td>
</tr>
<tr>
<td>Fujisawa sintered Fo$_{90}$</td>
<td>Synthetic</td>
<td>Al, Ca, Mn, Zn</td>
</tr>
<tr>
<td>LLNL “Fo80” (Fo$_{85}$)</td>
<td>Synthetic</td>
<td>Al, Ca, Cr, Mn, Co?, Ni?</td>
</tr>
<tr>
<td>Springwater olivine Fo$_{82}$</td>
<td>Natural</td>
<td>Ca, Cr, Mn</td>
</tr>
<tr>
<td>LLNL “Fo67” (Fo$_{70}$)</td>
<td>Synthetic</td>
<td>&lt;none&gt;</td>
</tr>
</tbody>
</table>

Shankland from ORNL
LLNL olivines from George Rossman, Boyd and Fujisawa from Caltech
San Carlos and Springwater olivine from Smithsonian
## Olivine Standards: Mn, Fe, Ni

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-olivine GRR-392</td>
<td>Synthetic</td>
<td>Fe</td>
</tr>
<tr>
<td>Mn-olivine RDS P-1087</td>
<td>Synthetic</td>
<td>Mg, Ca, Fe</td>
</tr>
<tr>
<td>Fayalite GRR-391</td>
<td>Synthetic</td>
<td>Mn</td>
</tr>
<tr>
<td>Fayalite RDS P-1086</td>
<td>Synthetic</td>
<td>Mg, Cr, Mn</td>
</tr>
<tr>
<td>Rockport Fayalite</td>
<td>Natural</td>
<td>Mg, Ca, Cr, Mn, Zn</td>
</tr>
<tr>
<td>Fayalite ORNL</td>
<td>Synthetic</td>
<td>Al?, Ca?, Cr</td>
</tr>
<tr>
<td>Ni-olivine P-877</td>
<td>Synthetic</td>
<td>Cr?, Fe, Co</td>
</tr>
</tbody>
</table>

GRR and RDS from George Rossman, P numbers Caltech probe standards
Rockport Fayalite from Smithsonian
Rockport Fayalite

- RF is widely used as primary Fe standard
  But Mg and Zn present, not in wet chemistry analysis
  [Low level oxides suspected to be variable not reported in wc analysis]
- Is ferric iron present? – apparently not:
  Wet Chemistry: Fe$_2$O$_3$ 1.32, FeO 66.36 %, Tot: 99.18
  Dyar XANES: RF iron is completely reduced.
- Grunerite in separate: Fe$_7^{2+}$Si$_8$O$_{22}$(OH)$_2$
- Magnetite at locality, in separate (Fe$_2^{3+}$Fe$_2^{2+}$O$_4$) ??
- Analysts should use EPMA analysis when using RF as primary standard.
### Fayalite Standards

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Rockport Wet Chemistry</th>
<th>Rockport EPMA</th>
<th>RDS P-1086 EPMA</th>
<th>GRR391 EPMA**</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>Not reported</td>
<td>0.046</td>
<td>0.385</td>
<td>0</td>
</tr>
<tr>
<td>SiO₂</td>
<td>29.22</td>
<td>29.99</td>
<td>30.04</td>
<td>(29.49)</td>
</tr>
<tr>
<td>CaO</td>
<td></td>
<td>0.045</td>
<td>0</td>
<td>0.004</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td></td>
<td>0.059</td>
<td>0</td>
<td>0.010</td>
</tr>
<tr>
<td>MnO</td>
<td>2.14</td>
<td>2.13</td>
<td>0.092</td>
<td>0.212</td>
</tr>
<tr>
<td>FeO*</td>
<td>67.55</td>
<td>67.62</td>
<td>69.61</td>
<td>(70.34)</td>
</tr>
<tr>
<td>NiO</td>
<td></td>
<td>0.007</td>
<td>0.012</td>
<td>0.011</td>
</tr>
<tr>
<td>ZnO</td>
<td>Not reported</td>
<td>0.575</td>
<td>0.006</td>
<td>0.007</td>
</tr>
<tr>
<td>Total</td>
<td>99.18</td>
<td>100.48</td>
<td>100.16</td>
<td>(100.04)</td>
</tr>
<tr>
<td>Σ M²⁺</td>
<td>1.999</td>
<td>1.982</td>
<td>1.979</td>
<td>1.999</td>
</tr>
<tr>
<td>Si</td>
<td>1.001</td>
<td>1.009</td>
<td>1.010</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Rockport WC: FeO 66.36, Fe₂O₃ 1.32, FeO* 67.55. TiO₂ 0.04, H₂O 0.1
EPMA: PAPF, olivine stds, Heinrich 1986 macs, 20KV, n=4  **GRR391 std Si, Fe**
Systematic Errors in Olivine $M^{2+}_2SiO_4$

PAPF, Heinrich 1986 macs @ 20 KV, 40 TOA

<table>
<thead>
<tr>
<th>Olivine Group</th>
<th>Standard Type</th>
<th>Analysis Total</th>
<th>$\sigma$, wt%</th>
<th>Si cations 1 ideal</th>
<th>$\sigma$</th>
<th>$\Sigma M^{2+}$ 2 ideal</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivines</td>
<td>Oxide</td>
<td>101.14</td>
<td>0.42</td>
<td>0.989</td>
<td>0.004</td>
<td>2.023</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td>Syn. Olivine</td>
<td>100.22</td>
<td>0.37</td>
<td>0.994</td>
<td>0.003</td>
<td>2.012</td>
<td>0.006</td>
</tr>
<tr>
<td>Fayalites</td>
<td>Oxide</td>
<td>100.93</td>
<td>0.20</td>
<td>0.990</td>
<td>0.001</td>
<td>2.022</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>Syn. Olivine</td>
<td>100.34</td>
<td>0.23</td>
<td>1.010</td>
<td>0.001</td>
<td>1.981</td>
<td>0.003</td>
</tr>
<tr>
<td>Mn,Ni Olivines</td>
<td>Oxide</td>
<td>99.32</td>
<td>0.33</td>
<td>0.991</td>
<td>0.003</td>
<td>2.018</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>Syn. Olivine</td>
<td>100.07</td>
<td>0.30</td>
<td>1.002</td>
<td>0.003</td>
<td>1.995</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Averages of total and cation stoichiometry for all olivines from test data set.
For olivines, $\text{Mg}/(\text{Mg+Fe}) = 0.860 \pm 0.080$ (ox) vs. $0.861 \pm 0.079$ (oliv).
Identical k-ratios corrected using PAP full $\Phi(\rho z)$ and Heinrich 1986 macs, relative to oxide vs. synthetic olivine standards.
Olivine Formula: $M^{2+}_2SiO_4$
Systematic Error Using Oxide Standards

Olivines: Oxide Standards / Syn. Olivine Standards
PAPF Heinrich 1986 macs 20 KV

Wt% Oxide in Olivine (MgO, SiO2, FeO)

Oxide Stds / Olivine Stds

- Mg Fayalite
- Fe Olivine
- Mg Olivine
- Si Olivine
- Si Fayalite, Mn,Ni Olivine
- Fe Fayalite

Oxide Stds / Olivine Stds

- Olivine SiO2
- Olivine MgO
- Olivine FeO
Status Report: EPMA of Olivine

- EPMA using synthetic olivine standards better than oxide standards:
  Superior analysis total, Si cation ~1.0, and $\Sigma M^{2+} \sim 2.0$
- Improvement in EPMA accuracy for olivine using
  Armstrong $\Phi(\rho z)$ coupled with FFAST mac data set.
- Using oxide standards we observe:
  Overcorrection of Mg and Fe in olivine across Fo-Fa binary
  Undercorrection of Si in low-Mg olivine (Fayalite, Mn-ol, and Ni-ol)
  Marginal underestimation of Mg/(Mg+Fe).
- These relationships extend to all MgFe silicates relative to composition.
- Alpha-factor analysis of systematic errors in Fo-Fa system:
  EPMA and wet chemistry of natural olivines are not internally consistent.
  Worst: Boyd Forsterite Mg and Fe not consistent (Caltech standard)
  Best: Springwater Mg,Fe, and Mg in San Carlos (Fe in SC less so)
Accuracy of EPMA:
Quantitative Analysis of Olivine
Olivine EPMA Accuracy Study:
Alpha factor method extended to olivine

- Alpha factor (α-factor) method used to evaluate:
  Systematic errors for Φ(pz) correction algorithms
  Internal consistency of EPMA-only data and EPMA vs. wet chemistry.

- Compositional end-members for α-factor systems:
  Pure elements     Mg – Fe, i.e., Ziebold-Ogilvie
  Pure oxides       MgO – FeO, i.e., Bence-Albee
  Olivine binary    Mg$_2$SiO$_4$ – Fe$_2$SiO$_4$

- Synthetic olivines, pure Fo and Fa, used as primary standards for α-factor analysis.
- Natural olivines require projection onto Fo-Fa binary for comparison.
- Anticipate decreased reliance on correction algorithm and fundamental parameters as one moves from pure element end members to olivine end members. Measurement errors ultimately control accuracy.
Olivine Alpha Factor Study: Comparison of Calculated and Measured Concentration

• Calculated $\alpha$-factors using $\Phi(\rho z)$ algorithms and mass absorption coefficients and a polynomial fit to the individually calculated values. C known, K calculated.

• Experimental $\alpha$-factors extracted from olivine analyses. K measured, C calculated.
  Compared with calculated $\alpha$-factors.
  If measurements, algorithms, and data sets are correct, all experimentally determined analyses would lie on theoretical lines.

• Wet chemistry data evaluated.
  K measured, C obtained from wet chemistry.
  If wet chemistry data, algorithms and data sets are correct, all wet chemistry analyses would also lie on the theoretical lines.
Extraction of $\alpha$-factors from Experimental Measurements

\[ \frac{C_{AB}^A}{K_{AB}^A} = \alpha_{AB}^A + (1 - \alpha_{AB}^A)C_{AB}^A \]

\[ y = b + mx \]

\[ K = (P - B)^{smp}/(P - B)^{std} \]

\[ \alpha_{AB}^A = \left[ \frac{C_{AB}^A}{K_{AB}^A} - C_{AB}^A \right] \frac{1 - C_{AB}^A}{1} \]

For olivine:
Forsterite: $C = \text{Wt Fraction MgO} / [\text{MgO in Mg}_2\text{SiO}_4]$  
Fayalite  $C = \text{Wt Fraction FeO} / [\text{FeO in Fe}_2\text{SiO}_4]$
Analysis of Mg Kα in Shankland Forsterite using MgO Std: Experimental Determination of α-factors

Bence-Albee Analysis of Forsterite for Mg Kα using MgO

C / K Data Mg Kα in SiO2 - MgO Shankland Forsterite

\[ y = -0.1909x + 1.1909 \]
\[ y = -0.1428x + 1.1428 \]
\[ y = -0.075x + 1.075 \]
MgO Std – Shankland Fo Mg Kα

Variation of α-factors with Composition, kV

Multiple kV Analysis Highlights X-ray Absorption Errors

Oxide Binary α-factors: SiO2 - MgO
Experimental Shankland Fo vs. φ(ρz)
Mg Kα in Olivine Using Forsterite Standard Calculated and Experimental Data, Effect of MAC’s

1. Historical overcorrection, esp. H66 at Fo-rich, FFAST macs reduce overcorrection.
2. Good agreement EPMA of syn. and natural olivines, esp. H86, Henke using Armstrong $\Phi(\rho z)$.
3. Boyd Forsterite Mg value of wet chemistry inconsistent with wc of San Carlos and Springwater.
Fe Kα A-factors in Fo-Fa Binary
Better accuracy compared to Mg

1. Minimal dependence on mac data set. Could calculate Mg by 2-Fe for binary olivines only.
2. Good agreement EPMA of syn. and natural olivines with Armstrong Φ(ρz).
3. Continuum fluorescence important for Fo-rich olivines.
4. Boyd Forsterite and San Carlos Fe value of wet chemistry least consistent with others.
### EPMA of San Carlos Olivine
**Correction Method and macks @ 20 KV, 40 TOA**

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Wet Chem Ox / H66</th>
<th>PDR Ox / H66</th>
<th>PAPF-1 Ox / H86</th>
<th>Arm-1 Ox / H86</th>
<th>PAPF-2 Ol / H86</th>
<th>Arm-2 Ol / H86</th>
<th>PAPF-3 Ol / FF</th>
<th>Arm-3 Ol / FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>49.42</td>
<td>50.10</td>
<td>50.04</td>
<td>49.82</td>
<td>49.44</td>
<td>49.44</td>
<td>48.98</td>
<td>49.00</td>
</tr>
<tr>
<td>SiO₂</td>
<td>40.81</td>
<td>40.74</td>
<td>40.66</td>
<td>40.07</td>
<td>40.56</td>
<td>40.58</td>
<td>40.34</td>
<td>40.69</td>
</tr>
<tr>
<td>FeO*</td>
<td>9.55</td>
<td>10.13</td>
<td>10.08</td>
<td>9.89</td>
<td>9.89</td>
<td>9.89</td>
<td>9.89</td>
<td>9.74</td>
</tr>
<tr>
<td>Total</td>
<td>100.29</td>
<td>101.66</td>
<td>101.47</td>
<td>100.47</td>
<td>100.60</td>
<td>100.60</td>
<td>99.90</td>
<td>100.12</td>
</tr>
<tr>
<td>Σ M²⁺</td>
<td>2.005</td>
<td>2.025</td>
<td>2.025</td>
<td>2.034</td>
<td>2.016</td>
<td>2.016</td>
<td>2.014</td>
<td>2.003</td>
</tr>
<tr>
<td>Si</td>
<td>0.997</td>
<td>0.986</td>
<td>0.986</td>
<td>0.982</td>
<td>0.991</td>
<td>0.991</td>
<td>0.992</td>
<td>0.997</td>
</tr>
<tr>
<td>Mg/(Mg+Fe)</td>
<td>0.902</td>
<td>0.898</td>
<td>0.899</td>
<td>0.900</td>
<td>0.899</td>
<td>0.901</td>
<td>0.898</td>
<td>0.900</td>
</tr>
</tbody>
</table>

PDR: Philibert-Duncumb-Reed ZAF, oxide stds, Heinrich 1966 macks  
PAPF-1 and Arm-1: Φ(ρz) algorithms, oxide stds, Heinrich 1986 macks  
PAPF-2 and Arm-2: synthetic olivine stds, Heinrich 1986 macks  
PAPF-3 and Arm-3: synthetic olivine stds, FFAST macks  
Same k-ratios, n=4, CaO 0.09, Cr₂O₃ 0.06, MnO 0.14, NiO 0.37 (wt %)  
Olivine Formula: $M^{2+2}_{\text{SiO}_4}$ [PFW 7/2004, PDR and PAPF algorithm errors corrected]
Effect of Tilting and Particle Effects
Inconel Spheres: Diameter ~ 30 um
Inconel Sphere EDS Spectra: Effect of Takeoff Angle

![Graph showing EDS spectra for Inconel Sphere at 15 kv, with energy in KeV on the x-axis and counts per 100 sec on the y-axis. The graph compares spectra taken at the top of the sphere, towards EDS, and away from EDS. Elements such as Al, Mo, Ti, Cr, Co, and Ni are identified with their L-lines.](image-url)
Inconel Sphere Low Energy EDS Region

Inconel Sphere 15kv

Counts per 100 sec

Energy, KeV

- Al
- Cr L
- Ni L
- Mo
- C

Toward EDS

Top of Sphere

Away from EDS

UO EPMA Workshop 2008
WinXray: EDS Spectra at 30, 40, 50 degree TOA

Calculated WinXray EDS Spectra NiCrAl System, 15 KV

Counts

Energy, KeV

NiCrAl 50 deg
NiCrAl 40 deg
NiCrAl 30 deg
Al Kα Peak Intensity at -10° to +10° Tilt Relative to 40°

![Calculated WinXray EDS Spectra NiCrAl System, 15 KV](image)
## Calculated Tilt Effect on Al-Cr-Ni Alloy Composition

<table>
<thead>
<tr>
<th>Takeoff Angle</th>
<th>Al Kα Intensity</th>
<th>Al Wt %</th>
<th>Cr Kα Intensity</th>
<th>Cr Wt %</th>
<th>Ni Kα Intensity</th>
<th>Ni Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>59.85</td>
<td>2.45</td>
<td>437.57</td>
<td>37.28</td>
<td>263.80</td>
<td>58.43</td>
</tr>
<tr>
<td>35</td>
<td>66.52</td>
<td>2.73</td>
<td>441.18</td>
<td>37.58</td>
<td>265.79</td>
<td>58.87</td>
</tr>
<tr>
<td><strong>40</strong></td>
<td><strong>72.21</strong></td>
<td><strong>2.96</strong></td>
<td><strong>443.95</strong></td>
<td><strong>37.82</strong></td>
<td><strong>267.31</strong></td>
<td><strong>59.21</strong></td>
</tr>
<tr>
<td>45</td>
<td>77.04</td>
<td>3.16</td>
<td>446.13</td>
<td>38.01</td>
<td>268.49</td>
<td>59.47</td>
</tr>
<tr>
<td>50</td>
<td>81.12</td>
<td>3.33</td>
<td>447.86</td>
<td>38.15</td>
<td>269.42</td>
<td>59.68</td>
</tr>
</tbody>
</table>

**Nominal**

GMR Thin Film program: calculate emitted intensity at each takeoff angle. (We don’t want k-ratio relative to standard at each takeoff angle)

X-ray intensity relative to 40 degree value used to scale weight %

- Al range 0.88 wt% / 20 degrees = 0.044 wt% per degree = 1.5% relative/deg.
- Cr range 0.88 wt%, = 0.12% relative/degree
- Ni range 1.25 wt%, = 0.063 wt% per degree = 0.11% relative/degree

Conclusion: 10 degree tilt error results in percent level analytical errors
Problem Systems
Problem Systems in EPMA:
Analytical Elements in Problem Matrices

• Analytical Problems:
  • X-ray peak overlaps
  • High x-ray absorption
  • Spatial issues, inhomogeneity
  • Particle, thin film, etc.

• Perform proper measurement to obtain correct k-ratio
• Use standard as close to sample for high correction analysis
• Necessary to evaluate all correction algorithms and mass absorption coefficients – do not blindly accept one pairing as the best
WDS Background Selection (Natural Peak Width) And High Order WDS Interferences

- Example AlCrNi alloy used in Lehigh Microscopy School lab
- WDS scan on pure Al necessary to establish full natural peak width
- People choose backgrounds too close to peak
  If background is not true on pure element, also not true on any sample
- Cr Kb IV reflection observed at Al Ka peak position on TAP
WDS Scan LIF: Al, Cr, Ni and NiCrAl Sample
Note background intensity as function of Z

Counts

Spectrometer position, mm LIF

Cr Kα 1,2

Cr std
NiCrAl
Ni std
Al std
WDS Scan LIF: Al, Cr, Ni, and NiCrAl Sample
Note background intensity as function of Z

Counts

10000
1000
100
10
1

Spectrometer position, mm LIFH

Ni Kα 1,2
Ni β 1,3

Ni std
NiCrAl
Cr std
Al std
WDS Scan TAP: Al, Cr, Ni, and NiCrAl Sample
Note Cr K$\beta$ IV-order interference on Al K$\alpha$, Full Al peak width

![Graph showing spectra for Al, Cr, Ni, and NiCrAl samples with Al K$\alpha$, Al K$\beta$, Cr K$\beta$, and Cr K$\alpha$ peaks and their respective satellites and IV-order interferences.](image-url)

- Al K$\alpha$ 1,2
- Al K$\beta$ Satellites
- Cr K$\beta$ 3 IV-order
- Cr K$\alpha$ 1,2 IV-order

Counts per sec vs. Spectrometer position, mm TAP
WDS Scan: LiF Crystal
95IRV Green, 95IRW Blue, 95IRX Red
WDS Scan: LiF Crystal
95IRV Green, 95IRW Blue, 95IRX Red
WDS Scan: PET Crystal
95IRV Green, 95IRW Blue, 95 IRX Red

Corning 95IRV, 95IRW, and 95IRX
PET 70 - 90 mm

Counts per sec

Spec pos mm
WDS Scan: PET Crystal
Si Kα limb and Hf Mβ Overlap on Rb Lα
WDS Scan: PET Crystal
Sr Lα Peaks, Rb Lβ family overlaps
WDS Scan: PET Crystal
Th Mβ on U Mα, K Kα Peaks & Ovlp U Mβ

Corning 95IRV, 95IRW, and 95IRX
P-10 Flow counter -- PET 116-134 mm

- U Mβ
- Th Mγ
- Ar K α edge
- U Mα
- Th Mβ
- Th Mα

Counts per sec
Spec pos mm
Elevated and Uncertain MAC Values for K, L, M Lines: Proximity to Absorption Edge of Matrix Element

<table>
<thead>
<tr>
<th>K-Lines and absorber for K, L, M edge</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>Be</td>
</tr>
<tr>
<td>Na, Zn, Nd</td>
<td>Mg, Na, Ge, Gd</td>
</tr>
<tr>
<td>K, Ar, Pd, Ac</td>
<td>Ca, K, Cd, U</td>
</tr>
<tr>
<td>Rb, Sc, Pb, Sr, Br, Po</td>
<td>Y, K, Rn, Zr, Rh, Ra, Nb, Sr, Th, Mo, Y, U, Te</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>L-Lines and absorber for K, L, M edge</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti, N, Sc, In</td>
<td>V, N, Ti, Sn</td>
</tr>
<tr>
<td>Cr, O, V, Sb</td>
<td>Mn, O, Cr, I</td>
</tr>
<tr>
<td>Fe, F, Mn, Xe</td>
<td>Co, F, Fe, Ca</td>
</tr>
<tr>
<td>Ni, F, Co, La</td>
<td>Cu, Ne, Ni, Ce</td>
</tr>
<tr>
<td>Zn, Ne, Cu, Nd</td>
<td>Ga, Na, Zn, Prm</td>
</tr>
<tr>
<td>Ge, Na, Ga, Eu</td>
<td>As, Na, Ge, Tb</td>
</tr>
<tr>
<td>Se, Mg, As, Dy</td>
<td>Br, Mg, Se, Er</td>
</tr>
<tr>
<td>Kr, Al, Br, Yb</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>M-Lines and absorber for K, L, M edge</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fr, S, Te, Po</td>
<td>Ra, As, Hg, Th</td>
</tr>
<tr>
<td>La, Ce, Sc, Xe</td>
<td>Pr, Ti, Cs</td>
</tr>
<tr>
<td>Nd, Ti, Cs</td>
<td>Pm, Ti, Ba</td>
</tr>
<tr>
<td>Sm, V, La</td>
<td>Eu, V, Ce</td>
</tr>
<tr>
<td>Gd, Cr, Pr</td>
<td>Tb, Cr, Nd</td>
</tr>
<tr>
<td>Dy, Cr, Prm</td>
<td>Ho, Mn, Sm</td>
</tr>
<tr>
<td>Er, Mn, Sm</td>
<td>Tm, Fe, Eu</td>
</tr>
<tr>
<td>Yb, Fe, Gd</td>
<td>Lu, Fe, Tb</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fr, S, Te, Po</th>
<th>Ra, Al, Kr, Lu, W, Al, Kr, Hf</th>
</tr>
</thead>
<tbody>
<tr>
<td>La, F, Co, Ba, Ce, Ne, Ni, La</td>
<td>Pr, Ne, Ni, Ce</td>
</tr>
<tr>
<td>Nd, Ne, Cu, Pr</td>
<td>Pm, Ne, Ni, Nd</td>
</tr>
<tr>
<td>Sm, Na, Zn, Prm</td>
<td>Ea, Na, Ga, Sm</td>
</tr>
<tr>
<td>Gd, Na, Ga, Eu</td>
<td>Tb, Na, Ge, Gd</td>
</tr>
<tr>
<td>Dy, Na, Ge, Tb</td>
<td>Ho, Mg, As, Dy</td>
</tr>
<tr>
<td>Er, Mg, As, Ho</td>
<td>Tm, Mg, Se, Er</td>
</tr>
<tr>
<td>Yb, Mg, Se, Tb</td>
<td>Lu, Al, Br, Yb</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fr, S, Te, Po</th>
<th>Ra, Cl, Te, At</th>
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<tr>
<td>La, F, Co, Ba, Th, Cl, Ru, Rn</td>
<td>Ce, Ne, Ni, La</td>
</tr>
<tr>
<td>Pr, Ne, Ni, Ce</td>
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<tr>
<td>Pm, Ne, Ni, Nd</td>
<td>Sm, Na, Zn, Prm</td>
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<tr>
<td>Ea, Na, Ga, Sm</td>
<td>Gd, Na, Ga, Eu</td>
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<tr>
<td>Tb, Na, Ge, Gd</td>
<td>Dy, Na, Ge, Tb</td>
</tr>
<tr>
<td>Ho, Mg, As, Dy</td>
<td>Er, Mg, As, Ho</td>
</tr>
<tr>
<td>Tm, Mg, Se, Er</td>
<td>Yb, Mg, Se, Tb</td>
</tr>
<tr>
<td>Lu, Al, Br, Yb</td>
<td></td>
</tr>
</tbody>
</table>
Example problem:
Identification of Ir-Si unknown
Mass Absorption Coefficients for Si Kα
By Absorber Z, All MAC Data Sets Compared

MAC for Si Ka by Z Absorber Elements

- Citzmu
- Linemu
- McMaster
- Mac30
- MacJTA
- FFAST

Atomic Number Z
Comparison of Si Kα MACS
Relative percent $\sigma$

MAC for Si Ka by Z Absorber Elements

Atomic Number $Z$

Percent Standard Deviation, Relative
Silicon Kα MAC at L-edge of Absorber

MAC for Si Ka by Z Absorber Elements

- Citzmu
- Linemu
- McMaster
- Mac30
- MacJTA
- FFAST

Atomic Number Z

MAC

0 1000 2000 3000 4000 5000 6000 7000

25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45
Silicon Kα MAC at M-edge of Absorber
Error Analysis Ta Lα in TaSi₂
All algorithms and MAC sets (PAPF-FFAST = 1.0)

Error Histogram Ta Lα in TaSi₂
Relative to PAP-FFAST Nominal K-ratios

$\Phi(\rho z)$ Models

Philibert-Duncumb-Reed
ZAF

Frequency

Kcorr / Kexp
Error Analysis Si Kα in TaSi₂
All algorithms and MAC sets (PAPF-FFAST=1.0)

Dramatic demonstration of choice of MAC data set:
Variation of Φ(ρz) models and 4 mac data sets

Kexp / Kcorr
## Calculated Compositions of TaSi$_2$
Relative to PAP—FFAST Nominal K-ratios

<table>
<thead>
<tr>
<th>PAPF with MAC</th>
<th>Wt% Si</th>
<th>Wt% Ta</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM</td>
<td>14.74</td>
<td>73.74</td>
<td>88.48</td>
</tr>
<tr>
<td>M30</td>
<td>15.64</td>
<td>74.02</td>
<td>89.66</td>
</tr>
<tr>
<td>(FFAST)</td>
<td>23.69</td>
<td>76.31</td>
<td>100</td>
</tr>
<tr>
<td>LM</td>
<td>24.87</td>
<td>76.52</td>
<td>101.39</td>
</tr>
<tr>
<td>MM</td>
<td>25.96</td>
<td>76.85</td>
<td>102.81</td>
</tr>
</tbody>
</table>
Conclusions

• Geological applications require multicomponent accuracy evaluation
• Use of $K_{\text{meas}}/K_{\text{calc}}$ plot used for data analysis, WDS and EDS
• CMASTF standards provide instrument calibration data set
• Experimental K-ratio data set available for development and testing
• Identification of inconsistent compositions
• Accuracy of analysis in CMASTF system better than 2%, precision limited
• SDD quantitative analysis data highly competitive with WDS
• Excellent prospects for high speed SDD quantitative analysis in particle, mapping applications